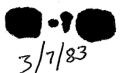
US ERA ARCHIVE DOCUMENT

	Date	Out	EFB:
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TO:

R. Mountfort

Product Manager 23

TS-767

FROM:

Emil Regelman,

Acting Chief

Review Section No. 1

Environmental Fate Branch Hazard Evaluation Division

Attached please find the environmental race review of:						
Reg./File No.: 10707-9						
Chemical: Acrolein						
Type Product: Herbicide						
Product Name: Magnacide H						
Company Name Magna Corporation						
Submission Purpose: Review data	to support label	amendment				
ZBB Code: Other	ACTION CODE: 30	5				
Date in: <u>1/24/83</u>	EFB # 161	<del>_</del>				
Date Completed: 3/7/83	TAIS (level II)	Days				
Deferrals To:	62	6				
Ecological Effects Branch		•				
Residue Chemistry Branch						
Toxicology Branch						

### 1.0 INTRODUCTION

Magna Corporation has submitted data in support of proposed label revisions for Magnacide H (Acrolein, as a. i.), EPA Reg. no. 10707-9, concerning storage and holding time of treated water. Magnacide H is currently registered (as a restricted use pesticide) for use as an aquatic herbicide for the control of submerged and floating weeds and algae in irrigation ditches.

Current general directions include the statements: "Do not permit dairy animals to drink treated water. Do not use where waters will either flow into or transfer via underground streams to potential sources of drinking water. Do not release treated water for 6 days after application into any fish bearing waters or where it will drain into them."

## 1.1 Chemical

Common name:

Acrolein

Chemical name:

2-propenal

Chemical structure:

 $CH_2 = CH - CHO$ 

### 2.0 DIRECTIONS FOR USE

Use directions are appended to this review. Maximum use rate yields water concentration of 15 ppm.

Labeling, including, "Magnacide H Application and Safety Manual," have been revised to contain the statement: "Make Application in such a manner that concentrations lethal to fish will not enter fish bearing waters." This proposed revison replaces the (above) statement relating to the 6 day restriction.

## 3.0 DISCUSSION OF DATA

EFB files indicate no environmental fate data have ever been submitted to support the registration of acrolein for this use.

Data submitted for review include:

3.1 Differential Pulse Polarographic Determination of Acrolein in Water Samples. L. H. Howe. Anal. Chem. 48(14) December 1976. Tab 2, paper 1.

This article describes an analytical method developed for analysis of acrolein using differential pulse polarography (DPP) with a dropping mercury electrode (DME). The detection limit is reported as 0.05 mg/l. Data were reported showing recovery at 0.1, 0.3, and 0.5 mg/l.

The author reports no statistical differences from samples analyzed by DPP and spectrometric determination of adsorbance at 600 nm. However, the article mentioned that other methods of analysis, including spectrometric determination, gave erroneous results.

### Conclusion

This study provides information about the development of an analytical method for determining acrolein. However, recovery data are necessary to complete the review of this study.

Note: EFB files contain the full report of this analytical method developed under an Interagency Agreement between the EPA and Tennessee Valley Authority. The author reported recovery of 97% (mean of seven determinations) for concentrations of 0.1 and 0.3 mg/L.

3.2 Polarographic Reduction of Aldehydes and Ketones. Part XXII. Reduction and Oxidation of <, & -Unsaturated Aldehydes: Acrolein, Tiglaldehyde and Substituted Cinnamaldehydes. Spritzer, L. and P. Zuman. J. Electroanal. Chem. 126 (1981). Tab 2. Paper 2.

This article provides additional theoretical information on the reduction of acrolein during polarographic analysis.

### Conclusion

This article presents information that EFB considers ancillary.

3.3 Determination of Acrolein in Aqueous Solutions by Differential Pulse Polarography. Brady, J. L. and D. L. Kissel. Magna Corporation. Tab 2. Paper 3.

This report describes, presumably, the analytical method used in subsequent studies submitted on the dissipation of acrolein.

# Conclusion

This study is incomplete. Data on sample recovery need to be submitted. The registrant should clarify whether this is the method of analysis used in the field monitoring studies submitted. The descriptions in in those studies are not sufficiently detailed.

3.4 Analysis of Acrolein in Aged Aqueous Media. Comparison of Various Analytical Methods with Bioassays. C. L. Kissel, et. al. J. Agric. Food Chem. 26(6) 1978.

#### Procedure

A stock solution of acrolein was diluted to a 5% (0.749 M) solution with various buffer solutions (pH 5, phthalate; pH 7, phosphate, phosphate with yellow dye, and tris(hydroxymethyl)aminomethane (Tris);

pH 9, borate and Tris. The solutions were maintained in the dark at  $22 \pm 2$ °C. Aliquots were taken a various time intervals.

These stock solutions were analyzed by various methods:

Derivatization: bromide-iodide-thiosulfate titrimetric method, the 2,4-dinitrophenylhydrazine (DNPH) colorimetric method and the aminophenol fluorescence method.

Direct: UV, GLC, NMR, differential pulse polarography (DPP) and direct fluorescence.

Also, bioassays were conducted: ATP photometry, aerobic bacteria plate count, and a bluegill sunfish bioassay study using natural water taken from Clear Creek Tunnel, Trinity County, California.

## Results

Bioassays indicated that acrolein completely hydrolyzed within 150 hours at pH 5, 120-180 hours at pH 7, and 5-40 hours at pH 9 at 22 °C.

UV analysis provided no useful data. Extraneous peaks were observed.

Data obtained from NMR, DPP and direct fluorescence closely matched data obtained from the bioassay (Tables III and V). Data from derivatized analytical methods did not parallel the bioassay (Table IV).

Different values of acrolein were obtained from different analytical methods. The authors suggest that hydrolysis products could interefer with the analyses of some methods. The authors mention that the compound, 5,6-dihydro-2H-pyran-3-carboxaldehyde, has been reported as a hydrolysis product of acrolein.

The authors report that, in the fish bioassay, the level of acrolein remained constant at 0.8 ppm over the 7 day period. However, it was reported that other data (fish toxicity studies) support a concentration of 0.08 ppm (not 0.8 ppm as suggested by the aminophenol fluorescence analytical method used).

## Conclusions

EFB considers this study ancillary. This study is unacceptable as satisfying the hydrolysis data requirement.

Bioassays are not acceptable as indicating half-life as metabolites are not measured. EFB does not accept bioassay data as validating analytical data.

There was poor agreement in the results from the various analytical methods used in the report.

	•					time, h			
system	method	pН	0	3	24	48	120	144	240
potassium hydrogen phthalate	ATP	5	100		52 -	40	11	0	0
potassium dihydrogen phosphate	ATP <sup>a</sup>	7	100		77	61	24	11	0
potassium dihydrogen phosphate with dye	ATP.	7	100		69	46	0	0	0
tris(hydroxymethyl)aminomethane	ATP	7	100		75	43	20	-8	Ö
sodium borate	ATP	9	43	26	0.				_
tris(hydroxymethyl)aminomethane	ATP <sup>3</sup>	9	49	24	0				
potassium hydrogen phthalate	ATPb	5	100		92	77	38	20	0
potassium dihydrogen phosphate	ATPb	7 .	100		80	80	28	12	Ö
potassium dihydrogen phosphate with dye	ATP <sup>b</sup>	7	100		75	71	14	0	Ô
tris(hydroxymethyl)aminomethane	ATP	7	100		95	75	47	43	Ŏ
sodium borate	ATPb	9	51	33	0				-
tris(hydroxymethyl)aminomethane	ATPb	9	50	32	0				
potassium hydrogen phthalate	platec	5 .	100		84	60	11	2	Ö
potassium dihydrogen phosphate	platec	7	100		69	30	0	-	
sodium borate	platec	9	98	10	0			•	
potassium hydrogen phthalate	tubed	5	100		90-	80	25	10	0
potassium dihydrogen phosphate	tu bed	7	100		83	62	5	0	
sodium borate	tubed	9	100		25	0		-	-

<sup>&</sup>lt;sup>a</sup> Use concentration, 10 ppm. <sup>b</sup> Use concentration, 50 ppm. <sup>c</sup> Use concentration, 10 ppm, average number of aerobic colonies per sample 4.5 x 10<sup>a</sup>. <sup>d</sup> Use concentration, 10 ppm. Average number of sulfate colonies per sample 4 x 10<sup>a</sup>.

Table IV. Percentage of Accolein Remaining in Various Buffer Systems vs. Time, as Measured by Derivatization Methods

						tin	ne, h			30
system	method	рĦ	2	7	24	48	96	144	240	days
potassium hydrogen phthalate	titrimetric <sup>a</sup>	5		<del></del>	78	62	40	27	18	3
potassium dihydrogen phosphate	titrimetrica	7		•	66	43	27	20	18	3
tris(hydroxymethyl)aminomethane	titrimetrica	7			88	76	68	59	52	8
sodium borate	titrimetrica	9	72	52	34	29	28	26	24	10
tris(hydroxymethyl)aminomethane	titrimetrica	9	93	74	43	30	28	27	25	12
potassium hydrogen phthalate	colorimetricb	5	96		95	90	88	85	78	75
potassium dihydrogen phosphate	colorimetric	7	72		58	55	42	38	29	28
potassium dihydrogen phosphate with dve	colorimetric <sup>b</sup>	7	70		63	64	47	46	30	31
tris(hydroxymethyl)aminomethane	colorimetric <sup>5</sup>	. 7	78		72	73	72	61	50	36
sodium borate	colorimetric <sup>5</sup>	9	43	24	22	20	• 4	O.	50	16
tris(hydroxymethyl)aminomethane	colorimetricb	9	56	35	35	27				18
potassium hydrogen phthalate	fluorometric	5	99		99	99	98	95	90	78
potassium dihydrogen phosphate	fluorometrice	7	96		94	92	87	72	64	50
potassium dihydrogen phosphate with dve	fluorometrice	7	95		93	92	84	77	63	48
tris(hydroxymethyl)aminomethane	fluorometrice	7	97		95	96	95	91	84	68
sodium borate	fluorometric	9	70	63	33	30		J.L	0%	7
tris(hydroxymethyl)aminomethane	fluorometrice	9	92	85	. 78	72				10

a Iodide-bromide-thiosulfate reagents. b DNPH method. c m-Aminophenol method.

Table V. Percentage of Acrolein Remaining in Various Buffer Systems vs. Time, as Measured by Direct Methods

•				time, h			30	
system	method	pН	2	24	48	144	days	
potassium hydrogen phthalate	GLC	5	99	90	88	85	76	
potassium dihydrogen phosphate	GLC	7	95	91	87	73	48	
ootassium dinydrogen phosphate with dye	GLC	7	93	87	83	62	44	
ris(hydroxymethyl)aminomethane	GLC	7	99	90	87	79	63	
odium borate	GLC	9	72	28	18	• •	9	
ris(hydroxymethyl)aminomethane	GLC	9	90	60	43		10	
otassium hydrogen phthalate	NMR	. 5		72	55	17	8	
otassium dihydrogen phosphate	NMR	7		<b>5</b> 5	37	8		
otassium dihydrogen phosphate with dye	NMR	Ţ	-	55	39	8	6 8 8 12	
ris(hydroxymethyl)aminomethane	NMR	7		78	60	22	0	
odium borate	NMR	9	60	21	15	22	10	
ris(hydroxymethyl)aminomethane	NMR	9	88	38	22		14	
otassium hydrogen phthalate	polarographa	5	98	83	68	20	. 6	
otassium dihydrogen phosphate	polarographa	7	97	67	42	7	1	
otassium dihydrogen phosphate with dve	polarographa	7	97	68	43	÷	•	
ris(hydroxymethyl)aminomethane	polarographa	7	98	84	80	47	E .	
odium borate	polarograph <sup>a</sup>	9	62	9	4	4	. 1	
ris(hydroxymethyl)aminomethane	polarograph <sup>a</sup>	9	78	33	11	3	1	
otassium hydrogen phthalate	fluorometrico	5	97	96	98	94	9ô	
otassium dihydrogen phosphate	fluorometrico	7	52	27	. 30	< 0.1	90	
ootassium dihydrogen phosphate with dye	fluorometricb	7	52	25	2	<0.1		
ris(hydroxymethyl)aminomethane	fluorometricb	7	62	64	41	40	26	
odium borate	fluorometric	9	< 0.1	< 0.1	4.1	40	. 20	
ris(hydroxymethyl)aminomethane	fluorometric	9	4	<0.1	< 0.1		_	

Differential pulse mode. Direct method.

3.5 "Monitoring Acrolein in Naturally Occurring Systems." C. L. Kissel, et. al. Magna Corp.

### Procedure

Samples of four naturally occurring field waters were fortified with acrolein at various concentrations:

Water System	PPM Fortification Level
Oil field floodwaters Water C Water O	49 (C-49)*, 151 (C-151) 17 (Q-17), 49 (Q-49), 151 (Q-151)
Commercial Cooling tower Water P	10 (P-10)
Commercial irrigation project Water T	1.3 (T-1.3)

<sup>\* (-)</sup> represents water system-fortification listing used in tables.

Samples were stored at 22° C. Aliquots were taken at various times and analyzed by several methods: colorimetry (DNPH), GLC, UV spectroscopy, m- aminophenol fluorescence (APF), and differential pulse polarography  $\overline{\text{(DPP)}}$ .

Analysis was also by bacteria and fish bioassays (using field water T and rainbow trout). Fish were added to the water 10 minutes; 24, 48, 72, and 192 hours after acrolein was added.

The sulfide scavenging properties of acrolein were also measured as a part of this study.

### Results

The analytical method which measured acroelin directly suggest that acrolein does dissipate in natural water systems presumably maintained under laboratory conditions.

Residue data reported, based on analysis by various analytical methods, gave poor agreement for samples taken after 6 hours incubation. Also, it appears that concentration has an effect on results when analyzed by methods using derivatization steps. See Table 2.

It appears that differential pulse polarography (DPP) is the analytical method of choice by the registrant (since it correlates with bioassay

Table 2. Comparison of Various Actor lein Analytical Methods.

The letter denotes the water system, the numeral denotes the initial acrolein concentration (ppm)

bAbreviations for these methods are: m-aminophenal fluorescence (APF), dinitrophenylhydrazine colorimetry (DNPH), differential pulse palarography (DPP), gas liquid chromatography (GLC), ultravialet spectroscopy (UV).

Table 4. Fish Bioassay Data for System T-1.3.

Result of a 5 fish account	All fish died within 25 minutes All fish died within 5 hours All fish survived 24 hours
Time (h)	0.2 24 48 72 192 blank

<sup>a</sup>Time the acrolein solution was allowed to age before performing the bioassay.

results). However, for one study using irrigated water treated at 1.3 ppm (T-1.3 analyses) the registrant reported that the reliability of the DPP data during the later stages of hydrolysis is questionable (since it did not parallel the bioassay results).

### Conclusion

This study is considered as ancillary data.

Data reported for the analytical methods measuring acrolein directly suggest that acrolein does dissipate in natural water systems which EFB assumes were maintained under laboratory conditions. However, this study does not satisfy the aerobic aquatic metabolism study since sediment was not used in the study.

This study does not satisfy the hydrolysis data requirement. Natural water, not sterile distilled water, was used in the study.

Data reported on bioassays cannot be used to determine half-life of acrolein.

Residue data reported based on various analytical methods gave poor agreement for samples taken after 6 hours (Table 2)

The results of this study are inconclusive. Analytical methods which measure acrolein directly appear to follow the decline of biocide activity as measured by the bioassays. However, the results of bioassays cannot be used to confirm analytical results.

The study did not determine degradation products of acrolein in aqueous solutions.

The data on the sulfide scavenging properties of acrolein was not reviewed.

EFB notes this study mentions that hydrolysis of acrolein appears to produce carbonyl compounds (e.g. 5,6-dihydro-2H-pyran-3-carboxahdehyde). However, such data have not been submitted to EFB for review.

# 3.5 Actual use studies

These reports are a compilation of field monitoring trials in which the concentration of acrolein present in the "wave" as it moved down the irrigation canal was analyzed by differential pulse polarography.

- 3.5.1 Acrolein in Irrigation Waterways. Gaddis, C. W. and C. L. Kissel. Magna Corp. Proc. EWRS 6th Symposium on Aquatic Weeds. 1982. Tab 4.
- 3.5.2 Magna Corporation Inter-Office Memo. Acrolein Monitoring, Belridge Irrigation District. August 1, 1980. Tab 5. Paper 1.

- 3.5.3 Magna Corporation Inter-Office Memo. Acrolein Monitoring-Salt River Project, Grand Canal, Phoenix, Arizona. October 6, 1980. Tab 5. Paper 2.
- 3.5.4 Magna Corporation Inter-Office Memo. Acrolein Monitoring, Maricopa Water District Canal, Maricopa County, Arizona. Oactober 7, 1980. Tab 5 Paper 3.
- 3.5.5 Magna Corporation Inter-Office Memo. Acrolein Monitoring-Stine Canal Kern County, California. October 8, 1980. Tab 5. Paper 4.
- 3.5.6 Magna Corporation Inter-Office Memo. Magnacide H R In Imperial Irrigation District. July 31, 1981. Tab 5. Paper 5.
- 3.5.7 Magna Corporation Inter-Office Memo. Magnacide H R in Imperial Irrigation District-Follow Up Studies. Tab 5. Paper 6.

### Conclusion

These studies are considered as ancillary data. While they show that dissipation occurs, they provide little information or data upon which EFB can evaluate the environmental fate of acrolein.

Half-lives for acrolein residues in the individual canals cannot be calculated from the data submitted. Samples were not taken to a point were residues were non-detectable.

Applications were not at the maximum use concentration (15 ppm).

Acrolein concentration was measured on site using differential pulse polarography. Most of the papers provided a calibration curve. However, no recovery of spiked samples were reported.

The authors reported that on-site analysis was preferred since samples held of any length of time showed variable results. This was attributed to the high rate of hydrolysis occurring with acrolein.

3.5.8 Magna Corporation Inter-Office Memo. Magnacide H in IID's Trifolium 14 Lateral. August 4, 1982.

#### Procedure

The Trifolium 14 irrigation lateral was divided into 3 sub-sections to simulate holding ponds. As water flowed into the lateral, acrolein was metered into the flow. As ponds filled, the gates were closed separating each from the other, thus, creating three static state ponds. See Figure 1.

Water samples were taken during the filling period and at time intervals from six sampling locations in the ponds. Acrolein residues were measured off-site but within 15 to 20 minutes travel time of the test site. Water samples were chilled in ice during transport. Analysis was by differential

pulse polarography (DPP). Additional analysis was conducted with a field monitoring kit using 2,4-DNPH colorimetric analysis.

Water in the ponds ranged from 1.5 to 4.5 feet in depth and about 5 feet across.

A fish bioassay study was also conducted in pond 3 by pumping water from the pond into, through, and out of an aquarium. When analysis showed acrolein levels at 1 ppm, channel catfish were placed in the tank and observed.

#### Results

The temperature during the test period ranged from 28.3 to 29.4°C.

The registrant reports an initial rapid build up of acrolein concentration in water. After 28 to 30 hours the acrolein levels had declined to less than 50 ppb (The level at which the author reports acrolein is non-toxic to fish). See Table 1 and Figures 3 - 8.

Results of the 2,4-DPNH colorimetric method analysis are given in Table 2. Analysis show higher levels than those analyzed by DPP. Note: In other studies using this field kit, it was noted this kit did not appear to accurately monitor levels of acrolein after several half-lives.

The more rapid decline in pond no. 1 (sample sites 1 and 2) was attributed to water leakage from the pond around the gate.

Fish bioassay showed that 3 catfish added after 30.5 hours aging were still alive 3.5 hours later (Table 3). Polarographic analysis of the water reported 0.03 ppm acrolein residues after 30.5 hours aging and 0.04 ppm after 31 hours aging. All fish added at earlier intervals died. This was attributed to acrolein toxicity. See Table 3.

# Conclusion

The data presented in this study indicate that acrolein dissipates in water held in the field simulating holding ponds. However, this study alone does not provide adequate data upon which EFB can evaluate the environmental fate of acrolein.

No degradation products were identified nor was soil sediment analyzed.

The application was not at maximum use rate (15 ppm).

## 3.6 Additional actual use studies

Magnacide H monitoring Program for the State of Nebraska. Preus, M. W. and C. L. Kissel. Magna Corporation. August 31, 1982.

This report is a compilation of field monitoring trials conducted

# FIGURES FROM EPA ACC. # 249308

FIGURE 1
IMPERIAL IRRIGATION'S
TRIFOLIUM LATERAL 14

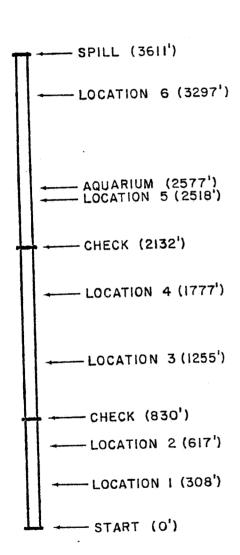


FIGURE 2
CALIBRATION CURVE IN TRIFOLIUM 14

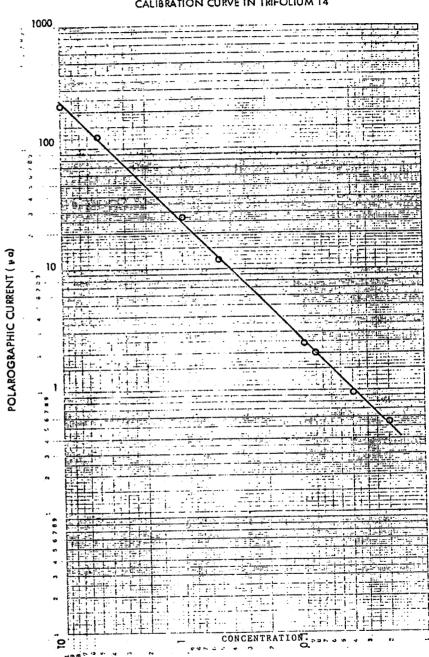


TABLE 1

# Acrolein Concentrations in Imperial Irrigation's Trifolium Lateral Number 14 as Determined by Differential Pulse Polarography

Location	•	Concentration (ppm)	Location	Time (h)	Concentration (ppm)
;	0	0	.4	0	
,	0.5	0.5	4	0.5	.0
	1	10.5	4	1	10.7
	1.5	9.0	i	1.5	7.5
	2	11.2	À		9.4
!	3.5	10.3	7	2	8.5
I	4	7.7	4	3	7.5
1	6	1.7	7	3.5	6.0
1	8	0.068	7	4	5.8
ì	12	0.065	4	6	5.0
			4	.8	5.0
2	0	0	4	.12	3,3
2	0.5	10.7		17	2.8
2	1	9.6	4	18	3.4
2	1.5	8.1		21	2.6
2	2	8.9	4	23	2.8
2	3.5	9.9	4	24	1.3
2	4	11.2	4	28.5	0.02
2 2 2 2 2 2 2 2 2 2 2	6	7.7	-		
2	8	4.0	5	0	0
2	12	0.02	5	0.5	4.4
		0.02	5	1	9
3	0	^	5	1.5	8.6
3	0.5	0	5	2.5	8.2
3	1	10	5	4	6.7
3	1.5	5.6	5	6	4.7
ă	2	9	5	8	4.5
3 3 3 3 3		9	,5	12	3.1
3	3.5 4	8.1	5	18	2.6
3		6.5	5	19	2.8
3	6	7. <b>2</b>	5	20.5	3.2
3	8	5	5	23	
3	12	4.5	5	23.5	2.5
3	16.5	4.0	5 5 5 5 5	25.5	1.4
.J	19	.3	5	26.5	0.16
<u>ر</u>	23.5	2.4	5	28.5	0.5
3	26	0.4	5		0.02
3 3 3 3 3 3 3	27.5	0.28	•	30	0.02
3	28.5	0.028			

# - TABLE 1 CONTINUED -

# Acrolein Concentrations in Imperial Irrigation's Trifolium Lateral Number 14 as Determined by Differential Pulse Polarography

			e rolarography		·
Location 6 6 6 6 6 6 6 6 6 6 6 6 6 6 6 6	Time (h)  0 0.5 1 1.5 2 2.5 3.5 4 6 8 12 18 19 21 23 24.5 26 28.5 30	Concentration (ppm)  0 1.2 8.5 7.6 6.7 7.7 6.4 5.5 4.0 4.5 2.6 2.7 2.4 2.6 0.7 0.34 0.55 0.1 < 0.02	Location Aquarium Aquarium Aquarium Aquarium Aquarium Aquarium Aquarium Aquarium Aquarium	Time (h)  25.5 26 26.5 27 27.5 28 30.5 31	Concentration (ppm)  0.5 0.33 0.11 0.13 0.15 0.24 0.03 0.04

Acrolein in Imperial Irrigation's Trifolium Lateral 14 as Determined by DNPH Colorimetry

			,		
Location	Time (h) 0 0.5 1 1.5 2 3.5 4 6 8 12 0 0.5 1 1.5 2 3.5 4 6 8 12 0 0.5 1 1.5 2 3.5 4 6 8 12 0 0.5 1 1.5 2 3.5	Concentration (ppm)  0 12 12 12 12 12 12 12 12 12 12 12 12 12	Location  4 4 4 4 4 4 4 5 5 5 5 5 5 5 5 5 6	Time (h)  0 0.5 1 1.5 2 3.5 4 6 8 12 18 19 21 23.5 0 0.5 1 1.5 2 3.5 4 6 8 12 19 21 19 21	Concentration (ppm)  0 12 12 12 12 11 10 11 8 8 8 8 8 11 10 11 11 8 8 8 8
3 3 3 3 3 3 3 3 3 3 3 3 3 3 3 3 3 3 3	0.5 1 1.5 2	12 12 12	5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5	6 8 12 19	11 8 8

# TABLE 2 CONTINUED -

# Acrolein in Imperial Irrigation's Trifolium Lateral 14 and Determined by DNPH Colorimetry

Location	Time (h)	Concentration(ppm)
.6	, 0	0
6	0.5	•
6	1	12
6	1 =	12
6	1.5	12
6	2	12
	3.5	12
6	4	,,
6	·6	''
.6	8	9
6	12	8
6		8
	18	6
6	19	6
.6	21	
6	23.5	6
6	25	4
	2.3	4

0

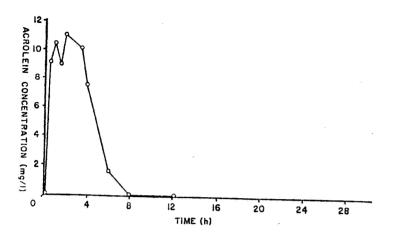
0

FIGURE 4

ACROLEIN IN IMPERIAL IRRIGATION'S TRIFOLIUM LATERAL 14, LOCATION 2

ACROLEIN IN IMPERIAL IRRIGATION'S TRIFOLIUM LATERAL 14, LOCATION I

FIGURE 3



ACROLEIN CONCENTRATION (mg/l)

TIME (h)

ACROLEIN IN IMPERIAL IRRIGATION'S

TRIFOLIUM LATERAL 14, LOCATION 4

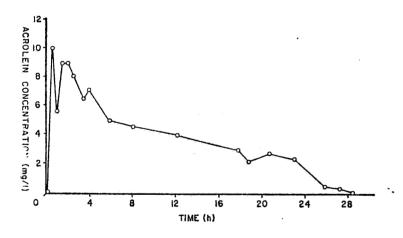
20

24

28

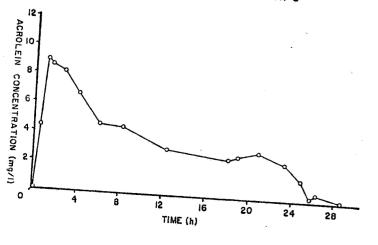
ACROLEIN IN IMPERIAL IRRIGATION'S TRIFOLIUM LATERAL 14, LOCATION 3

FIGURE 5



ACROLEIN CONCENTRATION (mg/i)

ACROLEIN IN IMPERIAL IRRIGATION'S TRIFOLIUM LATERAL 14, LOCATION 5



ACROLEIN IN IMPERIAL IRRIGATION'S TRIFOLIUM LATERAL 14, LOCATION 6

ıż

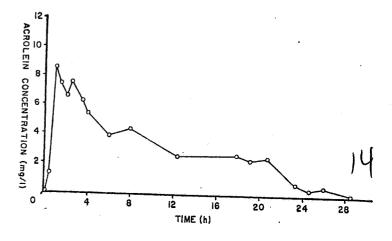
TIME (h)

16

20

24

28



# TABLE FROM EPA ACC. #249308

TABLE 3

CALIFORNIA DEPARTMENT OF FISH AND GAME AQUARIUM DATA(1)

FISH/COMMENTS	TIME (h)	TEMP °C	DISSOLVED OXYGEN PPM (2)	Added Magna D. MAGNACIDE H PPM (3)
ADD 1 CCF 1 MORTALITY NO MORE FISH ADDED UNTIL	18.75 19.75 ACROLEIN	- 28.5 CONC. A	6.5 6.4	(2.6 at site 5)
ADD 1 CCF 1 MORTALITY ADD 1 CCF CCF ALIVE AERATION OF AQUARIL	25.5 26.2 27 27.5 M STARTI	31.5 31.5 31.7 32.8	6.2 6.4 5.7 5.3	0.5 0.33 0.13 0.15
1 MORTALITY, ADD 1 CCF 1 MORTALITY, ADD 3 CCF ALL CCF ALIVE ALL CCF ALIVE 3 MORTALITY, ADD 3 CCF ALL CCF ALIVE	28 28.5 29.0 29.5 30 30.5 31.0 31.5 32.0 32.5 33	33.1 33.5 33.6 33.8 33.5 34.0 33.7 33.7 33.7 33.3	5.7 5.9 5.1 4.4 4.5 4.3 4.3 4.5 5.0 5.2?	0.24    0.03 0.04  

- (1) DATA SUPPLIED BY JOHN NELSON CDF&G
- (2) OXYGEN MEASURED IN AQUARIUM
- (3) RELATIVE MAGNA DATA

CCF = CHANNEL CATFISH 6-8" LONG

in Nebraska to support a special local need (SLN) registration for the use under a state registration with a 36 hour holding period (rather than the 6 day period on the current national label).

# 3.6.1 Magnacide H in the Ainsworth District Bone Canal

### Procedure

Magnacide H was metered into the Bone Canal of the Ainsworth Irrigation District for a concentration 0.5 mg/L.

This canal divides into two laterals 0.9 miles from the application site. The Airport Lateral travels 16 miles before draining into a creek. The Bone Lateral drains into a pond after 25.5 miles. At 3.8 miles the Sand Draw Lateral splits from the Bone Lateral and travels an additional 11.8 miles. The Bone Lateral can drain into a creek at 8.7 and 17.1 miles. See Figure 9.

Water samples were taken at approximately 150-200 yard below application site, at the Bone/Airport Lateral split and at points down these two arteries. Water velocity was 1.1 miles per hour.

Analysis was by differential pulse polarography. Sensitivity of the method was listed as down to 0.01 mg/L. DPNH colorimetric method sensitivity was to 0.5 mg/L.

# Results

The authors report that acrolein was found at 7.3 miles from the application site (FAS) in the Bone Lateral at 0.14 mg/L but was not detected at 10.4 miles or any other point down stream. In the Airport Lateral, acrolein was reported present at 4.1 miles FAS at 0.26 mg/L and at 0.03 mg/L at 6.2 miles FAS. It was non-detectable at 11.4 miles FAS. See Tables 4 and 5.

The authors report these data suggest a nine hour lifetime for acrolein in this canal system.

# 3.6.2 Magnacide H in the Bostwick District Franklin Main Canal

### Procedure

Magnacide H was metered into the Franklin Main Canal of the Bostwick District for a concentration of  $1.9 \pm 0.1 \, \text{mg/L}$ . The canal is 45 miles long and drains into a river. Sampling points were located at 8, 16, 25 and 33 miles FAS. See Figure 10.

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	Magnacide H (mg/l)	Polarograph	0	0.5	0.47	0	o	7	0.42	0.11			0	0	9.28	0.16	0		0	0.034	0		0	0	0	0	0	•	0		d Airport Lateral			/ Judica 467 a fue		,			/	بمر	)	Drain (16 miles)	>	1	8-12 (16.5 miles)	1	1	\ [
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Long Pine

Water flowing through furrows in a bean field 1.7 miles FAS was also sampled. Treated water was diverted from the canal, through the irrigation emitter, into the field and was allowed to reach the end of the furrows.

Analysis was by differential pulse polarography. Method sensitivity was reported to be 0.005 mg/L (levels to 0.001 mg/L could be observed). DNPH colorimteric method could not detect levels below 0.5 mg/L.

### Results

The authors report that acrolein was found 16 miles FAS at 0.07 mg/L and at non-detectable levels at other points FAS. See Table 6.

Acrolein levels decreased as the water moved toward the end of the furrow.

The authors report the data suggest a 19 hour lifetime for acrolein in this canal system. Also, the data suggest that field diversion could serve as a means of dissipation of acrolein residues. See Table 7.

3.6.3 Magnacide H in the Farmers Irrigation District Laterals No. 2165 and 2832.

### Procedure

Magnacide H was metered into two laterals, No. 2165 and 2832.

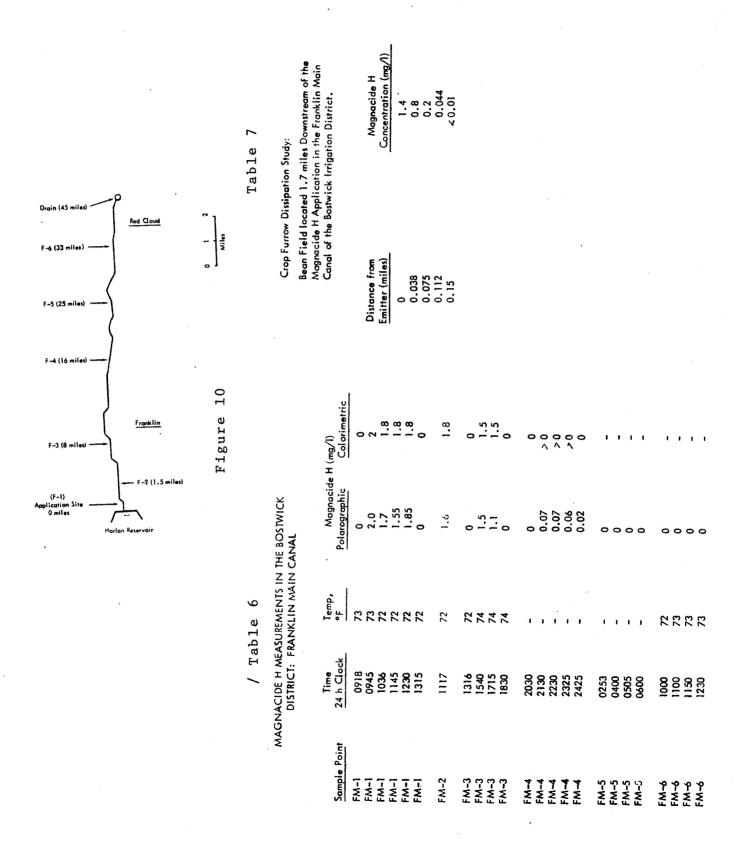
Lateral 2165: Magnicide H was metered into the lateral at a concentration of 3.2 mg/L. Lateral 2165 is 6.5 miles long and spills into a fish-bearing drain which continues and empties into Nine Mile Creek. At the 3.5 mile mark, the lateral traverses a series of 4 drops, each about 3 vertical feet. See Figures 11 and 12.

Water samples were taken 2 miles (F-2), 3.5 and 3.6 miles (F-3 and F-4, before and after the falls) and at 5.1 and 5.9 miles FAS. Samples were also taken 50 yards into the drain and 150 yards into Nine Mile Creek.

Lateral 2832: Magnacide H was metered into the lateral at a concentration of 4.9 mil/l. Lateral 2832 is 3 miles long and drains into a non-fish bearing canal. The water travels one mile before spilling into fish-bearing water.

Water samples were taken 150 yards down FAS, 0.9 miles (F-9), 2.0 (F-10) and 3.0 (F-11) miles FAS. A sample was also taken 1/4 mile into the canal.

TABLE, FIGURE FROM EPA ACC, # 249308



Analysis of acrolein was by differential pulse polarography, with sensitivity to 0.005 mg/l. The DNPH colorimetric kit could measure acrolein to 0.5 mg/l.

### Results

Lateral 2165: The author reports that acrolein was detected in the drain (6 miles FAS) at 0.04 mg/L (due to high dilution, 20X). It appeared that 0.6 mg/L was lost from the water in the lateral as it passed through the drops, presumably due to aeration. See Table 8.

Lateral 2832: The author report that approximately 1 mg/L acrolein was detected in the lateral prior to draining into the canal. Howerver, due to the dilution (70X), no acrolein was detected in the canal itself. See Table 9.

The authors report the acrolein lifetime in Laterals No. 2165 and 2832 were 10 hours and 6 hours, respectively.

Note: EFB notes the author mentions the usual practice in the District is to close the Laterals during application and drain the treated water into a field.

# 3.6.4 Magnacide H in the Frenchman-Cambridge District Red Willow Canal

# Procedure

Magnacide H was metered into the Red Willow Canal in two locations. The Canal is 24 miles long and drains into a dry creek which eventually joins the Republican River. See Figure 13.

The initial application, 2.4  $^+$  0.2 mg/L, was made 24 miles upstream from the drain. The second application, 2.1  $^+$  0.2 mg/L, applied about 4 hours later was located 9 miles downstream from the first application.

Water samples were taken 100 yards down from the initial application site, at the location of the second application and at the drain (into the dry creek).

Analysis was by differential pulse polarography, at a detection limit of 0.01 mg/L. The DNPH colorimetric method could not detect acrolein below 0.1 mg/L.

### Results

The author reports that the lifetime of the first application is 23 hours. It never reached the drain. Acrolein was found at 0.4 mg/L at the drain from the second application. The lifetime of the second application is reported to be 18 hours. See Table 10.

The author reports that no measurements were made in the dry creek. Most likely, no dilution would occur in the dry creek. Any residues would be dissipated before draining into the Republican River.

# 3.6.5 Magnacide H in Frenchman-Cambridge District Meeker Canal

## Procedure

The Meeker Canal is 39 miles long leading from a reservoir and empties into the Republican River. See Figure 14.

Magnacide H was applied at three locations along the Canal. The initial application of  $2.45 \pm 0.25$  mg/L was made at the base of the reservoir. The second and third applications were located 23 miles and 31 miles downstream, respectively.

Water was sampled 100 yards downstream from the initial application site. The passage of the first application was measured at the second application site and the passage of the first two applications was measured at the third application site. The final sampling site was at the drain junction of the Canal and Republican River.

Analysis was by differential pulse polarography with detection limit of 0.01 mg/L. The DNPH colorimetric method had detection limit of 0.1 mg/L.

# Results

The authors report that residues of the first and second applications did not reach the drain sampling site. The lifetimes were found to be 27 hours for the first application and 24 hours for the second. See Table 11.

Also, acrolein residues of 0.4 mg/L concentration was found at the drain sampling site as a result of the third application. The authors report that the half-life for the third application is 16 hours or less. See Table 1.

# 3.7.6 Magnacide H in Loup Basin District Farwell Main Canal

### Procedure

The Farwell Main Canal splits into the Farwell Main Canal and the Lower Farwell Main. Further on the Lower Farwell Main Canal splits into the Lower Farwell Main and the 2.2R Lateral. The Farwell Main Canal splits into the Farwell Main Canal and the 26.5 Lateral. See Figure 15.

Magnacide H was metered into the Farwell Main Canal at a 3.8  $\pm$  0.2 mg/L concentration 0.5 miles upstream from the initial split.

Water was sampled at various locations along the Canal and Laterals.

Dissipation of Magnacide was monitored in corn field furrows. At a point 0.1 mile downstream form pont F-4 on the Farwell Main Canal, water was allowed to flow through irrigation emitters and completely down the field furrows. Water was sampled as it flowed through the furrows.

Acrolein was measured by differential pulse polarography at detection limit of 0.01 mg/L. The DNPH method had detectable limit of 0.5 mg/L.

## Results

The author reports that Magnacide H had a lifetime of 27 hours in this system. See Table 12.

The author reports that the herbicide was detected at the drain of the Lower Farwell Main (4.9 miles FAS) and at the drain of the Farwell Main Canal (9 miles FAS) at concentrations of 1.0 mg/L and 0.3 mg/L, respectively. See Table 13.

Acrolein was found 50 yards into the drain of the Lower Farwell Main at 0.06 mg/L and was non-detectable 50 yards into the drain of the Farwell Main Canal.

Acrolein residues declined in the corn field furrows from a concentration of 2.3 mg/L to 0.62 mg/L after 0.2 miles of furrow. See Table 14.

St. Paul

F-10 ( 7 miles)

F-5 (3 miles)

-1 (0,5 mile)

Shermon Reservin

H (mg/l) Colorimetric 0 2.1 3.0 3.0		24	1101
Magnacide H (mg/l) Polarographic Colorimetric 0 1.35 2.1 2.7 3.0 3.1 3.0 0.03 0	0000000	0.052 0.72 1.05 0.9 0 0 0 0	0 0.13 0.31 0.16
Temp, °F 73 74 73 73 73 73			- - 71 Table 14
Time 24 h Clock 1420 1610 1706 1817	0010 0250 0455 0653 0820 1012 1320 1315	2400 0230 0455 0550 0638 0005 0305 0305 0305 0700 0830 1150 1150 1335 1335	0840 0950 1115 1220
Sample Point F-7 F-7 F-7 F-7	မာ့ ထု ထု ထု ထု ထို ထို ထု ထု ထု ထု ထု ထု ထို	6-7-7-7-7-7-10 6-7-7-7-7-10 6-10 6	7777
		•	

Table 12

MAGNACIDE H MEASUREMENTS IN LOUP BASIN DISTRICT: FARWELL MAIN CANAL

Figure 15

Drain (F-9) / 4.9 miles

F-7 (2.7 miles)

ģ

FR

O-- Drain (F-8) 5.3 miles

2.2R

Colorimetric

Polarographic

Time 24 h Clock

Sample Point

Magnacide H (mg/l)

4.6.6.0

3.6 3.7 0.7

6.4.6. 6.9.9.0

0.00

22222

2.0

Crop Furrow Dissipation Study:
Corn Field Located 3.1 miles Downstream of
Magnacide H Application in the Farwell Main
Canal of the Loup Basin Irrigation District.

•	Magnacide H Concentration (mg/l) 2.3 2.0 1.3 0.62	
	Distance from Emitter (miles) 0 0.07 0.13 0.2	

2.2.6 2.0.8 8.0

2.9

444

2.1 3.0 2.35

22242

1242 1435 1555 1715 1830

11111

3.5

2222

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5.3

TABLES, FIGURES FROM EPA ACC. # 249308

4444

1.45 2.6 2.35

Summary of Results From the Additional Actual Use Studies

Review Section	District	Length of canal* (Miles)	Initial conc. (ppm)	Level found**	Reported life times (Hours)
3.6.1	Ainsworth Airport Bone	16 26	0.5	ND @ 11.4 mi. ND @ 10.4 mi.	9 9
3.6.2	Bostwick	45	1.9	ND @ >16 mi.	19
3.6.3	Farmers 2165 2832	6.5 3.0	3.2 4.9	0.04 ppm @ 6 mi 1.0 ppm @ 3 mi.	
3.6.4	Frenchman- Red Willow (2 appl.)	24 15	2.4 2.1	ND @ 24 mi. 0.4 ppm @ 15 mi	23
3.6.5	Frenchman- Meeker (3 appl.)	39 16 8	2.45 "	ND @ 39 mi. ND @ 16 mi. 0.4 ppm @ 8 mi.	27 22 16
3.6.6	Loup-LFM "-FMC	4.9 9	3.8	1.0 ppm @ 4.9 m 0.3 ppm @ 9 mi.	

<sup>\*</sup>Distance from application site to last reported sampling site \*\*Distance from application site.

### Conclusions

While data show that acrolein dissipated, the studies alone do not provide adequate information upon which EFB can evaluate the environmental fate of acrolein.

Applications were not at maximum use rates.

Soil sediment was not analyzed nor were degradation products identified.

# 4.0 EXECUTIVE SUMMARY

- 4.1 The environmental fate of acrolein is not adequately understood.
- 4.2 The field monitoring studies that were submitted here show that the parent compound, acrolein, dissipates in the aquatic environment. However, these studies alone are not adequate for EFB to determine the environmental fate of acrolein and/or its degradation products.

- 4.3 EFB files indicate that no environmental fate data have ever been submitted to support this registered use of acrolein.
- 4.4 Additional data needed to support the proposed label revision include:

Hydrolysis study
Photolysis study
Soil metabolism study
Soil adsorption study
Fish accumulation study

- 4.5 Since field diversion could serve as a means of dissipation of acrolein residues, a field soil dissipation study will be required to assess the environmental fate of acrolein residues.
- 4.6 A rotational crop study will be necessary to determine if rotational crops take up acrolein residues as a result of crops grown in fields where treated water was diverted.
- 4.7 A field dissipation study conducted using the maximum use rate in a typical use area will also be necessary. Water should be diverted to a holding pond and sampled for residues.
- 4.8 Comments on the specific studies submitted for review are:
- 4.8.1 Recovery data should be provided for the differential pulse polarographic analytical method as used in analysis of acrolein in the field monitoring trials.
- 4.8.2 Degradation products must be identified since disappearance of parent alone is not adequate to determine environmental fate of a compound.
- 4.8.3 The discrepancies between the different analytical methods should be explained.
- 4.9 The registrant should be directed to the environmental fate guidelines for procedures and reporting requirements for conducting the above studies.

Clinton Fletcher

Review Section No. 1

Environmental Fate Branch

Hazard Evaluation Divison